METHOD OF TREATING THE SURFACE OF SUBSTRATES

The invention relates to a method of treating substrates, in particular a method of hydrophobizing or hydrophilizing the surface thereof.

Various surfaces, particularly metallic surfaces, tend to corrode in a moist environment and thus require protection therefrom.

Commonly used methods of passivating surfaces against corrosive attacks are oxidative treatments for forming oxide layers on surfaces, and phosphatizing or chromatizing treatments, in which case so-called conversion coatings are produced, which in the latter case consist of toxic chromates.

In the case of particles such as occur, for example, in metallic pigments in the form of aluminum flakes, it is difficult to produce an adequately dense coating using conventional processes, particularly because the coefficient of thermal expansion of the metal, in this case aluminum, differs from the coefficients of expansion of aluminum oxide so that the protective coating tends to form cracks when subjected to thermal stress.

When insufficiently protected surfaces are coated with paint or lacquer, blisters and corrosion products later form in a moist environment, *ie* the layer of lacquer or paint becomes detached from the corroding undersurface.

It is an object of the present invention to provide a method by means of which surfaces can be protected from corrosive attack and which avoids, in particular, the use of prior art processes and, in addition, is simple to use.

Furthermore, it is desired to create an organic layer which can have a coupling and compatibilizing effect on other organic layers.

Another object of the invention comprises the adjustment of the hydrophobicity or hydrophilicity of the surface to be coated.

The method of the invention achieves the object mentioned above by causing the substrate to be brought into contact with a solution of a polymer, which polymer exhibits UCST properties and is caused to be deposited onto the surface of the substrate as a layer by decreasing the temperature of the polymer solution.

Coating of the substrate may be partial, particularly with the formation of polymer islands; but the coat may alternatively be in the form of an all-over, uninterrupted layer.

The method of the invention shows greater advantages in achieving stabilization of particles against flocculation, particularly in non-polar media.

Polymers having UCST properties (referred to below as UCST polymers), precipitate from a polymer solution when the temperature of the latter falls below its critical temperature (UCST = upper critical solution temperature). This temperature depends on the particular solvent used for the polymer.

A description of UCST polymers and their properties is given in the monograph "Polymere" by Hans-Georg Elias, Huethig and Wepf-Verlag, Zug, 1996, pages 183 - 184.

The behavior of UCST polymers during temperature reduction of a polymer solution differs from the usual effect of precipitation of substances present in a saturated solution since reducing the temperature does not effect a gradual reduction in the solubility of the dissolved substance but causes, within a relatively narrow temperature range, drastic lowering of the solubility of the dissolved substance, *ie* the UCST polymer.

This property is utilized in the present invention to achieve deposition or separation of the UCST polymer onto a surface.

Preferred UCST polymers used in the present invention are selected from the group comprising polystyrenes, polyvinyl alcohols, polyvinyl pyrazoles, polyethylene oxides, polyacrylic acids, and derivatives thereof.

The solvent used is usually an organic solvent.

Preferably, the temperature of the solution of the UCST polymer in the solvent when it is brought into contact with the substrate surface is greater than the UCST, after which the temperature of the solution is reduced to a value in the UCST range or lower.

Since the UCST or the associated phenomena of deposition or change of solubility of the dissolved polymers show a certain bandwidth, it is possible to effect separation of the UCST polymer at temperatures ranging from *ca* UCST + 5 °C to UCST - 30 °C. While working in this temperature range it is possible to influence the layer thickness that can be obtained and, in particular, the density of the coating on the substrate surface, in a simple and favorable manner.

More preferably the temperature range in which the deposition of the UCST polymer onto the surface of the substrate is carried out is from T = UCST to T = UCST - 10 °C.

In this temperature range particularly dense layers of the UCST polymer are obtained on the surface of the substrate. Preferably, the temperature is maintained at the selected low level at which the UCST polymer separates until substantially complete separation of the UCST polymer from the solution onto the surface of the substrate has occurred.

Following separation of the UCST polymer onto the surface of the substrate, the surface of the substrate thus coated can be washed with a solvent for the UCST polymer at a temperature in the USCT range minus 10 °C or lower. With the temperature adjusted to this level the solvents can remove only those polymer molecules that are loosely deposited on the surface so that only the layer directly attached to the surface of the substrate remains. This avoids any undesirable de-

tachment of UCST polymers during subsequent treatment of the coated surface of the substrate, which might disturb the aftertreatment.

Using the method of the invention, it is possible to effect selective control of the hydrophobicity and hydrophilicity of the surface of substrates, and the degree of such control can be set within certain limits, for example, alone by selecting an appropriate UCST polymer.

The same effect as that attained by the washing step can be achieved by keeping the substrate together with the solution or solvent, following separation of the UCST polymer, for a short period, for example, *ca* 5 minutes, at a temperature above the UCST or above the temperature used for the deposition step, after which the substrate and solution are parted from each other. This has the same effect as the washing operation in that only those polymer molecules which are loosely deposited on the surface of the substrate or on the actual dense layer of UCST polymer are absorbed by the solvent and removed.

The preferred increase in temperature used in this step ranges up to 5 degrees above the UCST or the temperature used for deposition.

In order to obtain particularly secure coatings which also allow special freedom in subsequent processes regarding, for example, the choice of solvent used, provision may be made for immobilization, by a chemical reaction, of the UCST polymer layer after it has been deposited onto the surface of the substrate. Various reactions are possible in which UCST polymers can be used.

Alternatively, the polymer can be provided with active groups which can cause immobilization of the polymer. Examples of such active groups are carboxyl, amino, hydroxyl, and mercapto groups.

A particularly preferred UCST polymer for the purposes of the present invention is polystyrene. Modifications of polystyrene in precipitated form, which can at the same time cause immobilization or crosslinking of the polystyrene, are known from the literature by R. H. Boundy, R. F. Beuer "Styrene – Its Polymers, Copolymers and

Derivatives", Reinhold Publishers Corporation, New York 1952.

If immobilization of the coating of UCST polymer present on the surface of the substrate is carried out, the step of washing the surface of the substrate is preferably executed following immobilization.

The following process is particularly suitable for effecting immobilization:

- Deposition of a UCST polymer modified with double bonds followed by free radical crosslinking (initiated by UV light or radical formers).

Furthermore, the UCST polymer can be modified prior to or after deposition, in order to influence the hydrophobicity or hydrophilicity of the coating present on the surface and thus to exert very selective control on the hydrophobic or hydrophilic properties of the surface. This offers a further possibility of modifying the hydrophobizing/hydrophilizing effect over and above the choice of UCST polymer used.

For modification of the UCST polymer used to alter the hydrophobic properties, use can be made of the following methods:

- deposition of polar-modified or ionically modified UCST polymers (*eg*, with sulfo groups or with PEO-modified styrene) or nonpolar-modified UCST polymers (*eg*, polystyrene copolymers with butadiene);

- effecting modification following deposition (in the case of polystyrene by Friedel and Crafts acylation/alkylation).

Preferably, the UCST polymer is modified and at the same time immobilized after deposition thereof onto a surface.

Since the coating produced by the invention on the surface of the substrate exhibits a certain degree of elasticity, the difference in the coefficient of thermal expansion thereof from that of the underlying surface of the substrate can be readily compensated. The formation of cracks in the coating, such as is observed, for example, on

protective brittle oxide layers of aluminum oxide or silicon dioxide or on chromates, is avoided with certainty with the present method involving coating with UCST polymers.

The method of the invention is used for providing both particles and flat substrates with a surface coating.

When the substrate used is a particulate substrate, the UCST polymer used is preferably one having a molar mass of from 1,000 to 50,000 g/mol.

When the substrates used are flat substrates, the UCST polymer is one having a molar mass of from 1,000 to 500,000 g/mol.

Particulate substrates include a large variety of possibilities, for example, pigments, fillers, fibers, nano particles, particles of colloidal or micellar systems or alternatively the aforementioned lamellar particles used in metallic effect lacquers.

The method of the invention is particularly suitable for applying very thin layers, so-called nano layers, to a surface, which nano layers, despite their very slight layer thickness, can produce dense coverage of said surface.

The invention also relates to a surface bearing a coating of UCST polymer, which coating is produced by one of the methods of the invention discussed above.

Of particular significance are surfaces bearing a coating comprising a so-called nano layer and, in particular, those surfaces which are metallic surfaces.

Finally, the UCST polymers are selected such that their UCST is above the temperature at which the coated substrates will be later used. Preferably, the UCST of the polymers is 10 °C, more preferably 15 °C, above the operating temperature of the substrates. The measures described above achieve thermodynamic stabilization of the UCST polymers deposited onto the surface of the substrate.

Generally speaking, the layer thickness of the layer deposited on the surface can be

influenced by

a) carrying out the method of the invention a number of times in succession;
b) reducing the temperature to an appropriately low value below the UCST; and/or
c) using the dissolved UCST polymer in different concentrations.

The present invention assumes special significance for surface coating steel, galvanized steel, aluminum, or aluminum alloys.

The method of the invention can be repeated any number of times in order to increase the layer thickness of the deposited material on a surface. Particularly in the case of flat substrates, for which higher molar masses of the UCST polymers tend to be more favorable, a greater layer thickness is obtained per process step or deposition step.

This and further advantages of the invention are illustrated below in greater detail with reference to the examples and drawings. In the figures

Fig. 1 shows the angle of contact between water and surfaces which have been coated with differently modified UCST polymers according to the invention; and

Fig. 2 shows the results of a corrosion resistance test on surfaces coated in the manner herein proposed.

The invention will now be described with reference to an example in which a particulate substrate, namely a metallic pigment, is used. The coating of metallic pigment particles obtained in the process of the invention causes hydrophobization of the surface and thus lowers the water absorption of paints containing such pigment particles. This leads to a reduction in the formation of blisters in the layer of paint and to improved corrosion resistance and resistance of the coated metallic pigments to environmental factors (acid rain). Preference is given in this context to layer thicknesses ranging from 5 to 100 nm.

Example 1:

12 g of pigment (Big Resist E900, sold by Eckart) are dispersed at 800 rpm for a period of 30 min in 40 mL of a 3:1 v/v decane/cyclohexane mixture with thermostatic temperature control at 23 °C. The dispersion is then placed in a round-bottomed flask equipped with a reflux condenser and is heated to 65 °C. 5 mL of a 33 wt % strength solution (room temperature) of a polystyrene polymer modified with acrylic end groups (molar mass 12,000 g/mol, sold by Aldrich, UCST: *ca* 50-55 °C) in cyclohexane are added, and the resulting mixture is cooled to 35 °C and, following a period of 10 minutes, again heated to 65 °C. 2.2 mL of a 33 wt % strength solution of the polystyrene derivative are added (room temperature) and the mixture is cooled to 35 °C. It is then heated to 50 °C, filtered, and dried at room temperature.

Production of the pigmented paint for execution of the condensed water test according to DIN 50,017:

Example 2 and Comparative Example 1:

In each case, 1.4 g of treated metallic pigment of Example 1 and untreated pigment (Big Resist E900, sold by Eckart) are dispersed in 25 mL of a non-convertible single component polyester/polyacryl paint blend at 800 rpm for 15 min at 23 °C and applied to glass plates using a doctor blade giving a thickness of the moist layer of 200 μm. The plates are aired over a period of 12 h at room temperature and the layers of paint are dried for 30 min at 80 °C.

Confirmation of the decreased water absorption by execution of a condensed water test according to DIN 50,017:

After the layers have cooled to room temperature, the condensed water test specified in DIN 50,017 is carried out at 40 °C. Following a period of exposure of 94 h, the layer of paint produced using the commercial pigment (Comparative Example 1) showed twice as many blisters as the layer of paint produced using the pigment post-treated with polystyrene by the above method (Example 2).

In another example a flat substrate in the form of a sheet of aluminum was coated with a layer of UCST polymer and the coating then modified to adjust the hydrophobicity of the surface layer:

Example 3:

An aluminum plate (Al 99.5; dimensions 50 x 20 x 1.5 mm) is placed in a 50 mL screw cap jar together with 50 mL of a 1:4 chlorobenzene/decane mixture. 0.5 mL of a 33 % strength solution of a polystyrene polymer modified with acrylic end groups (molar mass 12,000 g/mol, sold by Aldrich; UCST from *ca* 50 ° to 55 °C) in cyclohexane are added and the mixture is heated until the polymer has dissolved (*ca* 50 - 55 °C). The mixture is cooled to 25 °C, and after 10 min it is again heated to 50 °C. After re-cooling to 25 °C, the aluminum plate is taken out.

For additional modification of the deposited layers, test pieces obtained as in Example 3 are each dipped in one of various reaction mixtures over a period of 2 h at 23 °C and then rinsed a number of times with distilled water and dried in a forced air oven for a period of 10 min at 80 °C.

Modification 1:
Immersion in a reaction mixture comprising 50 mL of a 1:4 chlorobenzene/decane mixture, 5 mL of a *ca* 2 % strength solution of anhydrous $AlCl_3$ in chlorobenzene, and 1 mL of propionic chloride.

Modification 2:
Immersion in a reaction mixture comprising 50 mL of a 1:4 chlorobenzene/decane mixture, 5 mL of a *ca* 2 % strength solution of anhydrous $AlCl_3$ in chlorobenzene, and 1 mL of crotonic chloride.

Modification 3:
Immersion in a reaction mixture comprising 50 mL of a 1:4 chlorobenzene/decane mixture, 5 mL of a *ca* 2 % strength solution of anhydrous $AlCl_3$ in chlorobenzene, and 1 mL of fumaric chloride.

Modification 4:
Immersion in a reaction mixture comprising 50 mL of a 1:4 chlorobenzene/decane mixture, 5 mL of a *ca* 2 % strength solution of anhydrous $AlCl_3$ in chlorobenzene, and 1 mL of acetyl chloride.

When the polystyrene is appropriately modified and a crosslinking reaction is carried out, the polymer can be irreversibly immobilized (for details on such modifying reactions see R. H. Boundy, Styrene – Its Polymers, Copolymers and Derivatives, Reinhold Publishers Corporation, New York, 1952). A polymer layer immobilized in this way can be readily freed from uncrosslinked polymer by rinsing with cyclohexane. The angles of contact between water and the resulting aluminum specimens of Example 3 are listed in Table 1 and graphically summarized in Figure 1. As may be seen from Figure 1, the angle of contact of water can be varied by the above method within a range of from *ca* 75 ° to 85 °.

Table 1

Specimen	Contact angle of water [°]
Unmodified aluminum	92.2
Coated polystyrene	81.5
Coated polystyrene, modification 1	76.8
Coated polystyrene, modification 2	70.9
Coated polystyrene, modification 3	73.6
Coated polystyrene, modification 4	73.2

The increased resistance to corrosion of the aluminum specimen coated with a relatively hydrophobic polystyrene layer compared with an uncoated aluminum specimen, or of a polystyrene-coated aluminum specimen additionally hydrophilized by the method involving modification 1, was examined by subjection of the specimens to a condensed water test (DIN 50,017, duration 10 h) and quantification by photometric means, based, in each case, on the uncoated specimen. The results are illustrated graphically in Fig. 2.

A higher luminosity value indicates less propensity of the specimen to corrosion. Thus the results shown in Fig. 2 show very good conformity with the results of the measurements of the contact angles (Figure 1). A greater contact angle measured for the aluminum post-treated with only polystyrene indicates greater hydrophobicity of the coating. Accordingly the corrosive effects are less pronounced than in the case of an additionally hydrophilically modified polystyrene (modification 1) .